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(71) Applicant(s)

General Electric Company

(Incorporated in USA - New York)

One River Road, Schenectady, NY 12345,
United States of America

(72) Inventor(s)

Timothy Brydon Burnell
James Anthony Cella
Judith Stein

(51) INT CL⁶

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(56) Documents Cited

GB 2137646 A EP 0495298 A EP 0210402 A
EP 0113849 A US 5286766 A US 5266631 A
US 4563498 A

(58) Field of Search

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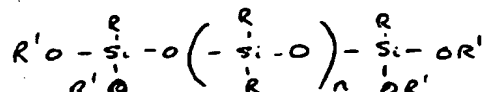
(74) Agent and/or Address for Service

Anne C Szary
GE London Patent Operation, Essex House,
12-13 Essex Street, LONDON, WC2R 3AA,
United Kingdom

(54) Low viscosity alkoxy polysiloxane compositions

(57) Low viscosity moisture curable silicone compositions useful to protect surfaces from biofouling are described and they comprise an alkoxy silane stopped polymer, a silica based filler and a condensation catalyst.

The alkoxy silane is preferably of formula



where each R and R' is an organic substituent and is preferably methyl.

These moisture cured compositions have a viscosity below 30,000 cps and a Mw of less than 100,000.

The compositions may be used as protective coatings and/or caulks/sealants and may be applied by spraying, brushing and troweling.

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LOW VISCOSITY SILICONE COMPOSITIONS

5 Field of the Invention

This invention relates to novel compositions of matter. More particularly, the instant invention is directed to low viscosity silica filled compositions which may be used to protect surfaces from
10 biofouling.

Background of the Invention

Structures exposed to water, whether fresh water or
15 seawater, often become encrusted with many objects and organisms. Such structures often include, among other things, ship hulls, buoys, splash-zone surfaces of oil production platforms and inlets and outlets of power stations. They become encrusted with, for example, objects
20 such as ice and organisms like barnacles, tube worms, algae and zebra mussels, all of which negatively impact the performance of the structures.

Moisture curable, 2-part silicone compositions have been employed as coatings to protect structures like the above-described from being encrusted with objects and organisms.
25 However, the conventionally employed silicone compositions consist of high molecular weight polysiloxanes and have high viscosities in the uncured state, making them very difficult to handle and apply. Because of this, such silicone compositions are often thinned with environmentally unfriendly organic solvents, making them easier to
30 handle and apply.

In an attempt to avoid the use of organic solvents, low viscosity compositions having low molecular weight silanol stopped

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polymers and non-reinforcing fillers have been made. However, these compositions are not desirable because they display poor physical properties in the cured state. In an attempt to increase their post-cure physical properties, these low viscosity compositions have
5 been mixed with silica. The resulting mixtures, however, display a dramatic increase in pre-cure viscosities; in fact, the viscosities of the mixtures are higher than those displayed in compositions having high molecular weight polyorganosiloxanes.

The instant invention, therefore, is directed to low
10 viscosity silica filled compositions that display favorable physical properties and foul release properties after curing.

Description of the Prior Art

15 Efforts have been described for preparing room temperature vulcanizable compositions. In commonly assigned U.S. Patent 4,959,407, solventless organopolysiloxane compositions are described and the compositions comprise a bis(ureido)silane as a coupler and an aminoxysiloxane as a crosslinker.

20 Additionally, in U.S. Patent 4,965,367, a process for preparing silacyclobutanes is described and the process comprises the step of reacting a halogen substituted silacyclobutane with a silylating reagent.

25 Still other investigators have focused on the preparation of curable compositions. In U.S. Patent 3,694,427, compositions comprising a silacyclobutane and an organopolysiloxane are described.

Summary of the Invention

30 The instant invention is directed to a sprayable composition comprising:

- (a) an alkoxysilane stopped polymer;
- (b) a silica based filler; and
- 35 (c) a condensation catalyst,

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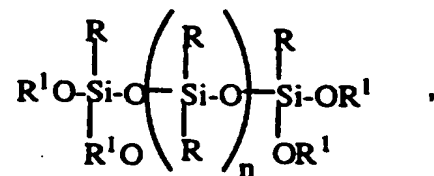
wherein the composition is volatile organic compound (VOC) free.

The compositions, unexpectedly, display a viscosity substantially identical to conventional low viscosity compositions such as those with low molecular weight silanol stopped polymers and non-reinforcing fillers like calcium carbonate. Moreover, they unexpectedly display viscosities which are at least about ten times and preferably at least about thirty times and most preferably at least about sixty times less than compositions with low molecular weight silanol stopped polymers and silica based reinforcing fillers. Low viscosity, as used herein, is defined to mean less than about 30,000 cps, preferably less than about 20,000 cps and most preferably less than about 10,000 cps at ambient temperature. Low molecular weight, as used herein, is defined to mean a Mw of less than about 100,000 and preferably less than about 60,000 and most preferably less than about 45,000.

Still further, the compositions of the instant invention unexpectedly show favorable physical properties after curing in comparison to conventional low viscosity compositions. The unexpected results of this invention are confirmed in the tables which follow below.

Detailed Description of the Preferred Embodiments

There is no limitation with respect to the alkoxysilane stopped polymers which may be employed in this invention. Often, however, they are represented by the formula



wherein each R is independently a C₁₋₁₀ alkyl group, C₁₋₁₀ alkoxy group, substituted or unsubstituted aromatic radical including a phenyl group, cyanoalkyl group including cyanoethyl, trihaloalkyl

group including trifluoropropyl or a vinyl group. Each R¹ is independently a C₁₋₁₀ alkyl group or substituted or unsubstituted radical. Preferably, however, each R is a methyl group and each R¹ is a methyl group. n is an integer from about 25 to 5,000 and
5 preferably has a value such that the viscosity of the alkoxysilane stopped polymers is about 100 to about 20,000 and preferably from about 200 to about 15,000 and most preferably from about 1,000 to about 10,000.

Such alkoxysilane stopped polymers are commercially
10 available and produced, for example, by reacting a silanol stopped polyorganosiloxane with a tri or tetrafunctional alkoxysilane in the presence of a capping catalyst.

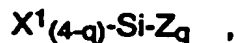
There is essentially no limitation with respect to the silica based fillers that may be employed in this invention. Often, however,
15 commercially available fumed silica is preferred.

There is also essentially no limitation with respect to the condensation catalysts which may be employed in this invention. Often they include salts of cerium, zinc and lead, including carboxylic acids thereof. The preferred catalysts are those which contain
20 titanium or tin, including dibutyltin-bis-acetylacetonate, dibutyltindilaurate and di-isopropoxybis-2,4-bis-pentanedionato titanium(IV).

The compositions of this invention may be prepared, for instance, in any mixing vessel capable of mixing the alkoxysilane
25 stopped silanol polymer, silica based filler and condensation catalyst. The order in which the reagents are mixed is generally not limited. Often, however, it is preferred to form a premix with the alkoxysilane stopped silanol polymer and silica based filler prior to adding the condensation catalyst.

30 In a preferred embodiment of this invention, it is desirable to add crosslinkers to accelerate curing. There is no limitation with respect to the crosslinkers which may be employed in the instant invention other than that they are capable of crosslinking alkoxysilane stopped polymers to produce a cured compositions. Th

often preferred crosslinkers employed in this invention are trifunctional organopolysilanes having the formula



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wherein each X^1 is independently a C_{1-10} hydrocarbon and preferably a methyl group and each Z is independently an alkoxy group including a methoxy group, aminoxy groups, dialkylamino groups including dimethylamino groups, oxime groups or alkoxy groups including methoxy groups and q is 3 or 4.

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Such crosslinkers are typically added to the above-described premix or to the condensation catalyst and can be prepared for instance by reacting a hydroxyamine or an alcohol with a silicone hydride. An additional description of crosslinker production

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may be found in commonly assigned U.S. Patent 4,959,407, the disclosure of which is incorporated herein by reference.

It is further within the scope of the instant invention to employ any conventional additives known in the art. Such additives include, for instance, oils, group IIA carbonates and sulfates like

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calcium carbonate and calcium sulfate, transition metal oxides like titanium and ferric oxides, carbon black, diatomaceous earth, alumina, hydrated alumina, glass microspheres, quartz, organic fillers as well as reinforcing and nonreinforcing fillers.

Additionally, it is within the scope of the instant invention to employ any of the conventional adhesion promoters known in the art. Such adhesion promoters include, for instance, nitrogen containing silanes such as 3-aminopropyltrimethoxysilane, 3-aminoethyltriethoxysilane and N-(2-aminoethyl-3-

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aminopropyl)trimethoxysilane, epoxide containing silanes such as 3-(glycidioxopropyl)trimethoxysilane and cyanurate containing silanes such as 1,3,5-tris(3-trimethoxysilylpropyl)isocyanurate.

30

There is no limitation with respect to the use of the novel compositions described in the instant invention; in fact, they may be employed, for example, as protective coatings and/or caulks/sealants.

Further, they may be applied via any conventional method including spraying, brushing and troweling.

The amount of alkoxysilane stopped silanol polymer, silica based filler and condensation catalyst employed in this invention is limited only to the extent that a curable composition is produced. Often, however, no more than about 20 parts by weight and preferably no more than about 15 parts by weight and most preferably no more than about 10 parts by weight of alkoxysilane stopped silanol polymer are employed for every part by weight of silica based filler.

Additionally, no more than about 10 parts and preferably no more than about 5 parts and most preferably no more than about 1 part by weight of catalyst is employed for every 100 parts of premix (mixture of alkoxysilane stopped silanol polymer and silica based filler) employed.

The following examples further illustrate and facilitate an understanding of the instant invention. The products obtained may be confirmed by conventional techniques such as proton and carbon-13 nuclear magnetic resonance spectroscopy, mass spectroscopy, infrared spectroscopy and GPC analysis.

Example 1

A mixing vessel was charged with 500g of a silane stopped polydimethylsiloxane (3000 centipoise at ambient temperature), 20g of methyltrimethoxysilane, 1.0g of sec-butylamine and 0.5g of acetic acid. The resulting mixture was heated to 60°C for 1 hour and cooled to about 45°C at which point 2.5g of hexamethyldisilazane were added as a methanol scavenger. The resulting polymer was an alkoxysilane stopped polymer, yield approximately 95%.

Example 2

5 A mixing vessel was charged with 10.0g of the
alkoxysilane stopped polymer produced in Example 1 and 0.1g of
dibutyltindilaurate. The resulting mixture was exposed to atmospheric
moisture under ambient conditions, became tack free within 1 hour
and cured to an elastomeric state after 10 hours.

Example 3

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Example 3 was conducted in a manner similar to the
one described in Example 2 except that di-isopropoxybis-2,4-bis-
pentanedionato titanium(IV) was used in lieu of dibutyltindilaurate.
15 The resulting composition became tack free within 1 hour and cured
to an elastomeric state after 10 hours.

Example 4

20 A mixing vessel was charged with 434.5g of
methyltrimethoxysilane stopped polydimethylsiloxane (3000
centipoise at ambient temperature) and 131g of
hexamethyldisilazane and octamethylcyclotetrasiloxane treated silica
which was added with stirring over five increments. When all of the
silica was added, another 434.5g of methyltrimethoxysilane stopped
25 polydimethylsiloxane were added. The resulting mixture was
subjected to vacuum for about 5 minutes and subsequently a high
shear mixer for approximately 2000 cycles. The resulting composition
was a low viscosity composition (about 7000 centipoise at ambient
temperature) with a silica based reinforcing filler.

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Example 5

Example 5 was prepared in a manner similar to the one
described in Example 4 except that calcium carbonate was used in

lieu of silica. The resulting composition had a viscosity of about 7000 centipois at ambient temperature.

Example 6

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A mixing vessel was charged with 100g of alkoxysilane stopped as produced in Example 4, 3.0g of tetraethylorthosilicate and 0.65g of dibutyltin-bis-acetylacetonate. After mixing, the resulting composition was degassed by centrifugation, poured into molds and cured for analysis.

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Example 7

Example 7 was prepared in a manner similar to the one described in Example 4 except that approximately 10% by weight of the composition included silicon oil (polydimethylsiloxane, 20 centipoise at ambient temperature). The composition was sprayed onto a solid substrate and cured to an elastomer displaying favorable film properties.

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The data in Table I is provided to demonstrate the low viscosities of the compositions of this invention in comparison to the conventional compositions with silanol stopped polymers. All compositions were prepared in a manner similar to those described in the examples.

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Table I

Entry	Polymer ^a	Polymer ^b viscosity	Filler	Composition ^b viscosity
1	x	3,000	CaCO ₃	7,000
2	x	3,000	Silica	460,000
3	y	3,000	Silica	7,000

^ax = silanol stopped polydimethylsiloxane; y = alkoxysilane stopped polydimethylsiloxane.

^bCentipoise at ambient temperature.

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The data in Table II is provided to demonstrate the post-cure favorable properties of the compositions of this invention. All compositions were prepared in a manner similar to those described in the examples.

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Table II

Entry ^a	Filler, ^b amount	Tear ^f strength lbs/in	Tensile ^f stress psi	Tensile ^f strain %	Shore A ^f hardness
1	None	4.4	24.2	23.7	15
2	CaCO ₃ , 5%	7.70±0.4	48.5	69.5	18
3	CaCO ₃ , 9%	8.07±1.96	82.0	130.0	18
4	CaCO ₃ , 13%	9.73±0.85	94.2	131.0	18
5	CaCO ₃ , 29%	13.7±0.61	175.9	154.0	30
6	Silica 5%	11.5	102.9	120.0	21
7	Silica 9%	14.7±0.99	306.0	214.0	27
8	Silica 13%	21±0.91	396.4	203.0	30
9	Silica 13% ^c	1.23±0.53	206.0	163.0	23
10	Silica 13% ^d	25.3±1.4	296.0	204.0	32
11	Silica 13% ^c	28.4±3.73	296.0	196.0	28

^aAll entries prepared with alkoxysilane stopped silanol polymer as prepared in Example 1.

^bAmount = weight % based on total weight of composition.

^cSilicon oil added, 20% based on total weight of the composition.

^d0.1 gram of di-isopropoxybis-2,4-bis-pentanedionato titanium(IV) added as in Example 2.

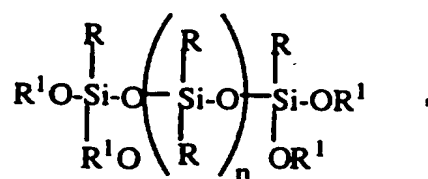
^eCoupler employed = 1,1-dimethoxysilacyclopentane.

^fAll pursuant to ASTM standards.

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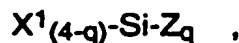
CLAIMS:

1. A sprayable composition comprising:
 - (a) an alkoxy silane stopped polymer;
 - (b) a silica base filler; and
 - (c) a condensation catalyst,
- 5 wherein the composition is volatile organic compound free and has a viscosity of less than about 30,000 centipoise at ambient temperature.
2. A composition in accordance with claim 1 wherein said alkoxy silane stopped polymer has the formula



- 5 wherein each R is independently a C₁₋₁₀ alkyl group, alkoxy group, substituted or unsubstituted aromatic radical, cyanoalkyl group, trihaloalkyl group or a vinyl group and each R¹ is independently a C₁₋₁₀ alkyl group or substituted or unsubstituted radical and n is an integer from about 25 to 5,000.
- 10 3. A composition in accordance with claim 2 wherein each R is a methyl group and each R¹ is a methyl group.
4. A composition in accordance with claim 1 wherein said silica based filler is a fumed silica.
5. A composition in accordance with claim 1 wherein said condensation catalyst comprises titanium or tin.
6. A composition in accordance with claim 5 wherein said titanium comprising catalyst is di-isopropoxybis-2,4-pentanedionato titanium(IV) and said tin comprising catalyst is dibutyltin-bis-acetylacetonate or dibutyltin dilaurate.
7. A composition in accordance with claim 1 wherein said composition has a viscosity of less than about 20,000 centipoise at ambient temperature.
8. A composition in accordance with claim 1 wherein said composition further comprises a crosslinker.

9. A composition in accordance with claim 8 wherein said crosslinker is a trifunctional organopolysilane having the formula



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wherein X^1 is a C_{1-10} hydrocarbon and each Z is independently an alkoxy group, aminoxy group, dialkylamino group, oxime group or alkoxy group and q is 3 or 4.

10. A composition in accordance with claim 1 wherein said composition further comprises additives.

11. A composition in accordance with claim 10 wherein said additives are oils, Group IIA carbonates and sulfates, transition metal oxides, carbon black, diatomaceous earth, alumina, hydrated alumina, glass microspheres, quartz or organic fillers.

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12. A composition in accordance with claim 1 wherein said composition further comprises adhesion promoters.

13. A composition in accordance with claim 12 wherein said adhesion promoters are 3-aminopropyltrimethoxysilane, 3-aminoethyltriethoxysilane N-(2-aminoethyl-3-aminopropyl)trimethoxysilane, 3-(glycidioxoxypropyl)trimethoxysilane or 1,3,5-tris(3-trimethoxysilylpropyl) isocyanurate.

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Application N : GB 9617490.9
Claims searched: 1-13

Examiner: Diane Davies
Date of search: 20 November 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3T

Int Cl (Ed.6): C08L 83/04

Other: Online: EDOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2137646 A (General Electric Co.) Whole document: moisture-curable siloxane composition having alkoxy substituted siloxane of formula (2) and silica filler (see page 5 lines 14-30).	1-13
X	EP 0495298 A (General Electric Co.) Whole document: RTV silicone composition having alkoxy terminated siloxane, reinforcing filler such as silica and tin condensation catalyst.	1-13
X	EP 0210402 A (Bayer AG) Whole document: preparation of siloxanes with alkoxy end-groups for use in RTV compositions with customary fillers.	At least claim 1
X	EP 0113849 A (General Electric Co.) Whole document: RTV composition having <i>inter alia</i> a siloxane terminated at both ends by a single alkoxy group, silica filler (see page 36) and catalyst.	1-13

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



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Applicati n N : GB 9617490.9
Claims searched: 1-13

Examiner: Diane Davies
Date of search: 20 November 1996

Category	Identity of document and relevant passage		Relevant to claims
X	US 5286766 A	(Shinetsu Chemical Co.) Whole document: low viscosity RTV silicone composition having alkoxy terminated siloxane, silica filler and titanium catalyst.	1-13
X	US 5266631 A	(Shinetsu Chemical Co.) Whole document: RTV silicone composition having alkoxy substituted siloxane, silica filler and condensation catalyst.	1-13
X	US 4563498 A	(General Electric Co.) Whole document: RTV composition having a siloxane terminated at both ends by at least two alkoxy groups, silica filler and catalyst.	1-13

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.